

A novel catalysis of *N*-hydroxyphthalimide (NHPI) combined with $\text{Co}(\text{acac})_n$ ($n = 2$ or 3) in the oxidation of organic substrates with molecular oxygen

Yasutaka Ishii *

Department of Applied Chemistry, Kansai University, Suita, Osaka 564, Japan

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Abstract

A novel class of catalysts for aerobic oxidation for a wide variety of organic substrates was developed. Benzylic compounds such as fluorene were oxidized with molecular oxygen in the presence of *N*-hydroxyphthalimide (NHPI) to give the corresponding oxygenated products such as fluorenone. For the oxidation of cycloalkanes, polycyclic alkanes and alkylbenzenes, which are difficult to be oxidized by NHPI alone, a combined catalytic system of NHPI with $\text{Co}(\text{acac})_n$ ($n = 2$ or 3) was found to be efficient for the oxidation of these substrates. Thus cycloalkanes were successfully oxidized with dioxygen in the presence of a catalytic amount of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid at 100°C to give cycloalkanones and dicarboxylic acids as principal products. Alkylbenzenes were also oxidized by this catalytic system to form the corresponding carboxylic acids and/or carbonyl compounds in good yields. Exposure of NHPI to atmospheric oxygen in benzonitrile at 80°C generated phthalimide *N*-oxyl (PINO), a key intermediate, in this oxidation. The formation of PINO from the NHPI and dioxygen was significantly accelerated by adding $\text{Co}(\text{acac})_2$ to the reaction system.

Keywords: *N*-Hydroxyphthalimide; Oxygen; Aerobic oxidation; Cyclohexane; Oxidation; Radical; Cobalt(II) acetylacetonate

1. Introduction

The selective oxygenation of saturated hydrocarbons is one of the most challenging and promising subjects in oxidation chemistry. In particular, homogeneous catalytic oxidation of hydrocarbons with molecular oxygen is very important in chemical industry. Several transition metal-catalyzed autoxidation have been applied to industrial processes (e.g., oxidation of cyclohexane, *p*-xylene, cumene, etc.) [1,2]. The finding of novel, selective oxidation catalysts

that utilize molecular oxygen as the primary oxidant is therefore an endeavor important to both synthetic and industrial chemistry. It has been reported that transition metals catalyze the oxidations of organic substrates by the combined use of molecular oxygen and reducing agents such as H_2 [3], NaBH_4 [4], RCHO [5], etc. Recently, halogenated metalloporphyrins have been shown to be efficient for the aerobic oxidation of alkanes [6].

N-Hydroxyphthalimide (NHPI) has first been used by Masui as an efficient electron carrier for the electrochemical oxidation of alcohols [7]. There has been a patent work on the oxida-

* Corresponding author.

tion of allylic hydrogen of isoprenoid with dioxygen using NHPI in the presence of a radical initiator [8].

In the course of our study on the oxidation of organic substrates with molecular oxygen, we found that NHPI is a unique catalyst for the aerobic oxidation for various substrates [9]. In this paper, we would like to report a novel catalysis of NHPI combined with metal salts such as $\text{Co}(\text{acac})_n$ ($n = 2$ or 3) in the oxidation of alkanes under relatively mild conditions [10,11].

2. Results

2.1. Oxidation of benzylic and hydroaromatic compounds with dioxygen catalyzed by NHPI

In order to evaluate the features of NHPI catalysis, the oxidation of fluorene (**1**) was examined under various reaction conditions. These results are shown in Table 1. Treatment of **1** in the presence of a catalytic amount of NHPI (10 mol%) in benzonitrile solution under oxygen atmosphere at 100°C for 20 h gave an oxidized product, fluorenone (**2**), in 80% yield. When the NHPI analogs *N*-hydroxysuccinimide (NHSI) and *N*-hydroxymaleimide (NHMI) were employed, **1** was oxidized to **2** in 62% and 41% yields, respectively (runs 4 and 5). However, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which serves as an efficient catalyst for the dehydrogenation of alcohols by dioxygen in the presence cupric chloride [12], has no catalytic activity (run 6).

To survey the generality of the present oxidation, various benzylic compounds were allowed to react in the presence of a catalytic amount of NHPI (10 mol%) under an atmosphere of oxygen (1 atm) at 100°C for 20 h (runs 7–15 in Table 1). For diphenylmethane and ethylbenzene, oxygenations took place at the benzylic positions to give the corresponding ketones in fair to good yields (runs 7 and 8). In the case of isopropylbenzene, with its tertiary carbon,

Table 1
Oxidation of benzylic derivatives with dioxygen catalyzed by NHPI^a

Run	Substrate	Catalyst	Yield (%) ^b
1		NHPI	(80)
2 ^c	1	NHPI	2 (15)
3	1	—	2 (trace)
4	1	NHSI ^d	2 (62)
5	1	NHMI ^e	2 (41)
6	1	TEMPO ^f	2 (0)
7		NHPI	(73)
8		NHPI	(34)
9		NHPI	(64) + (8)
10		NHPI	(20) + (30)
11		NHPI	(37) + (13)
12		NHPI	(42) + (7)
13		NHPI	(60)
14		NHPI	(83)
15		NHPI	(99)

^a Reaction conditions: substrate (2 mmol), NHPI (10 mol%), and PhCN (5 ml) at 100°C for 20 h.

^b GLC yields.

^c 80°C for 20 h.

^d NHSI: *N*-hydroxysuccinimide.

^e NHMI: *N*-hydroxymaleimide.

^f TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl.

demethylation took place in preference to hydroxylation to give acetophenone in 64% yield (run 9). In the oxidation of 1,1,1-triphenylmethane, 1,1,1-triphenylmethanol was obtained together with diphenylated product, benzophenone (run 10). Tetralin and indan were similarly oxygenated by this system, giving 1-tetralone (37%) and 1-indanone (42%), respectively, with small amounts of the corresponding alcohols (runs 11 and 12). It is interesting that oxygen-containing substrates such as benzyl

methyl ether, isochroman, and xanthene were smoothly oxidized by the NHPI–O₂ system to produce methyl benzoate, 1-isochromanone, and xanthone in 60%, 83%, and 99% yields, respectively (runs 13–15).

2.2. Oxidation of cycloalkanes with dioxygen catalyzed by NHPI combined with transition metals

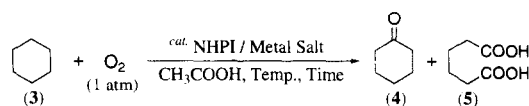
The oxidation of cyclohexane (**3**) to a cyclohexanone (**4**)/cyclohexanol (**6**) mixture (K/A oil) is the first step in the two-step process for the production of adipic acid (**5**). Although there are several variants of this oxidation, the principal method is the autoxidation of cyclohexane in the presence of a metal catalyst such as Co or

Mn salt [13,14]. An alternative cyclohexane oxidation uses a higher concentration of Co(III) acetate under oxygen pressure (20–30 atm) [15]. However, the homogeneous catalytic oxidations of **3** using these methods have several problems, e.g., oxidative attack on the C–H bonds is slow and requires vigorous reaction conditions. To overcome these limitations, a new catalyst for selective oxidation with dioxygen must be identified. Hence, the catalytic oxidation of **3** with atmospheric oxygen under mild conditions is a challenge in industrial catalysis.

The oxidation of **3** with dioxygen (1 atm) using a new catalyst, NHPI, under selected conditions was carried out. These results are shown in Table 2. Although a benzylic compound such as fluorene was efficiently oxidized to fluo-

Table 2

Oxidation of cyclohexane (**3**) with dioxygen catalyzed by NHPI combined with metal salts^a



Run	NHPI (mol %)	Transition metal	Temp. (°C)	Conv. (%)	Yield (%) ^b	
					4	5 ^c
1	10	—	100	1	trace	0
2	—	Co(acac) ₂	100	trace	trace	0
3	10	Co(acac) ₂	100	45	32	38
4	10	Co(acac) ₃	100	42	35	40
5	5	Co(acac) ₂	100	28	41	37
6	10	Co(acac) ₂	75	30	48	30
7	10	Co(acac) ₃	75	22	52	37
8 ^d	10	Co(acac) ₃	75	13	78	13
9 ^e	10	Co(acac) ₂	100	48	37	39
10 ^f	10	Co(acac) ₂	100	38	38	48
11	10	Co(OAc) ₂	100	43	31	44
12	10	Mn(acac) ₃	100	44	3	77
13	10	Cu(OAc) ₂	100	21	43	29
14	10	Fe(acac) ₃	100	5	90	trace
15	10	Ni(acac) ₂	100	0	—	—

^a **3** (5 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI and transition metal (0.5 mol%) in acetic acid (12.5 ml) for 6 h.

^b Based on **3** reacted.

^c Yield of dimethyl adipate after esterification with excess methanol.

^d Acetonitrile was used as a solvent.

^e Co(acac)₂ (1 mol%) was used.



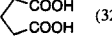






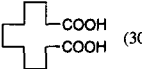



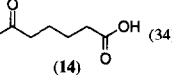

^f Co(acac)₂ (0.25 mol%) was used.

renone in high yield (80%) with molecular oxygen (1 atm) in the presence of NHPI (10 mol%) in benzonitrile at 100°C [10], **3** was not oxidized by NHPI alone under these conditions. Thus, the effects of several transition metal salts on the NHPI-catalyzed oxidation of **3** in a dioxygen atmosphere were examined. An initial survey of representative transition metals demonstrated that very small amounts of cobalt salts such as $\text{Co}(\text{acac})_n$ ($n = 2$ or 3) significantly facilitated the NHPI-catalyzed aerobic oxidation of **3** under moderate conditions. For example, the oxidation of **3** in the presence of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid at 100°C for 6 h (standard conditions) gave cyclohexanone **4** (32%) and adipic acid **5** (38%)

as the main products in the 45% conversion of **3** (run 3)¹. Oxidation did not take place in the absence of NHPI under these conditions (run 2). When $\text{Co}(\text{acac})_3$ was used in place of $\text{Co}(\text{acac})_2$ in this oxidation, **3** was converted to **4** and **5** at a slightly lower conversion (42%) (run 4). Similar effects of $\text{Co}(\text{acac})_2$ and $\text{Co}(\text{acac})_3$ on the oxidation of **3** were also observed at 75°C (runs 6 and 7). Oxidation was considerably retarded by the use of acetonitrile as a solvent, while the selectivity of **3** to **4** at 75°C was improved from

¹ By the GC-MS measurement of the reaction product of **3**, the formation of glutaric acid (up to 5%) and cyclohexyl acetate (up to 2%) other than **4** and **5** was confirmed.

Table 3
Oxidation of cycloalkanes with dioxygen catalyzed by the NHPI/ $\text{Co}(\text{acac})_2$ system^a

Run	Substrate	Conv. (%)	Yield (%) ^{b, c}		
1		46	 (27)	 (32)	
2 ^d	 (7)	93	 (8)	 (9)	 (10)
3 ^e	7	86	8 (53)	9 (17)	10 (16)
4 ^f	7	37	8 (63)	9 (8)	10 (17)
5		66	 (34)	 (30)	
6	 (11)	77	 (12)	 (13)	 (14)
7		30	Octanols (57)		Octanones (14)

^a Substrate (5 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid (12.5 ml) at 100°C for 6 h.

^b Based on substrate reacted.

^c Yield of dicarboxylic acid was estimated as dimethyl ester after esterification with excess methanol.

^d Reaction time was 3 h.

^e NHPI (5 mol%) was used.

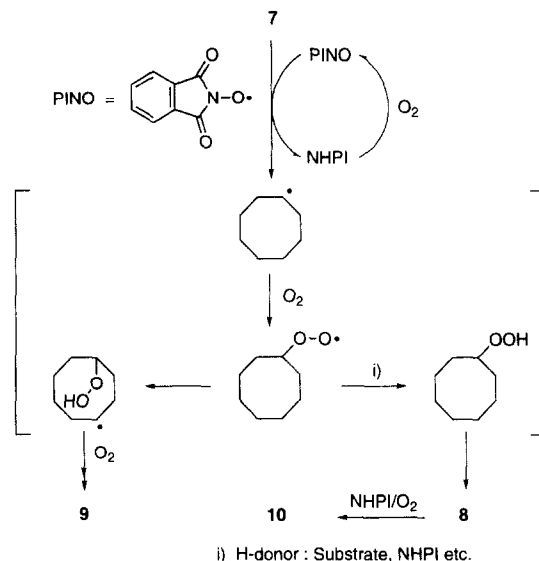
^f In the absence of $\text{Co}(\text{acac})_2$.

52% to 78% (run 8). Oxidation using $\text{Co}(\text{OAc})_2$ as a cocatalyst was similar to that with $\text{Co}(\text{acac})_2$ (run 11). $\text{Mn}(\text{acac})_3$, which is often used as a catalyst for autoxidation, was also effective in this oxidation. It is interesting to note that the addition of $\text{Mn}(\text{acac})_3$ led to **5** rather than **4** in high selectivity (77%). This oxidation was slightly enhanced by adding $\text{Cu}(\text{OAc})_2$. In contrast to the effect of Co and Mn salts in the NHPI-catalyzed oxidation of **3**, $\text{Fe}(\text{acac})_3$ had only a slight effect on the oxidation, and $\text{Ni}(\text{acac})_2$ had no effect.

When the quantity of NHPI was halved (5 mol%), **3** was oxidized at a slightly lower conversion (28%) to form **4** and **5** in 41% and 37% selectivities, respectively. However, the effect of the concentration of $\text{Co}(\text{acac})_2$ as the cocatalyst was clearly much less than that of NHPI. For the oxidation of **3** by NHPI (10 mol%) in the presence of $\text{Co}(\text{acac})_2$ (1 mol%) (run 9), the results were almost the same as those with 0.5 mol% of $\text{Co}(\text{acac})_2$ (run 3). It is noteworthy that the present aerobic oxidation of **3** resulted in **5** in higher selectivity, since the autoxidation of **3** in the presence of Co and Mn salts is known to lead to K/A oil (**4** and **6**) rather than **5** as the main product [13]. In particular, it is interesting that **3** was converted into **5** in one step in 77% selectivity by the NHPI/ $\text{Mn}(\text{acac})_3$ system under atmospheric oxygen at 100°C.

Based on these results, several cycloalkanes were oxidized under standard conditions, i.e., in the presence of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in an oxygen atmosphere (1 atm) using acetic acid at 100°C for 6 h (Table 3).

For the oxidation of cyclopentane under these conditions, the results were similar to those of **3** (run 1). However, cyclooctane gave 1,4-cyclooctanedione (16%) in addition to cyclooctanone (50%) and suberic acid (16%) in 93% conversion (run 2). Even when the amount of NHPI was reduced to 5 mol%, **8** was oxidized with a higher conversion (86%) (run 3). In contrast to **3**, which was slightly oxidized by NHPI alone, **7** could be oxidized to **8** (63%), **9**



Scheme 1. A possible reaction path for the oxidation of cyclooctane (**7**) with dioxygen catalyzed by NHPI.

(8%), and **10** (17%) in a 37% conversion by NHPI in the absence of any metals (run 4). The 1,4-diketone **9** is believed to be formed via intramolecular hydrogen abstraction by a transient peroxy radical generated from **7**, as will be discussed later (Scheme 1). Indeed, the successive oxidation of **8** under these conditions led to dicarboxylic acid **10**, while diketone **9** was not formed at all. Cyclododecane was also converted into the corresponding ketone and dicarboxylic acid at a satisfactory conversion (66%) (run 5). During the oxidation of these cycloalkanes, alcohols such as cyclohexanol and cyclooctanol are believed to be formed, but very small amounts of the corresponding acetates were detected using GC-MS. It is believed that these alcohols are easily oxidized to ketones and/or dicarboxylic acids since they are more reactive than the starting cycloalkanes. In fact, cyclohexanol **6** was oxidized to cyclohexanone **4** in 92% yield in acetonitrile at 75°C [11].

Methylcyclohexane (**11**) gave ketocarboxylic acid (**14**) as a major product along with 2-methylcyclohexanone (**12**) and 1-methylcyclohexanol (**13**) (run 6). The independent oxidations of **12** and **13** under these reaction condi-

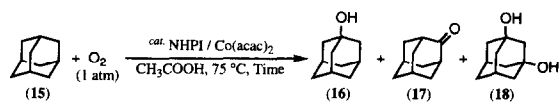
tions were carried out to reveal the reaction path to **14**. The oxidation of **12** gave **14**, while **13** was a less reactive substrate. Thus, **14** was a further oxidation product of **12**, but not of **13**. On the other hand, the oxidation of *n*-alkane such as *n*-octane by this system gave a mixture of 2-, 3-, and 4-octanols and the corresponding octanones (run 7).

2.3. Hydroxylation of polycyclic alkanes with dioxygen catalyzed by NHPI combined with $\text{Co}(\text{acac})_2$

There have been a few reports on the catalytic hydroxylation of adamantane (**15**) using O_2 as the ultimate oxidant [16]. In general, the direct hydroxylation of **15** with O_2 in the absence of any reducing agent such as aldehyde is very difficult to carry out in higher conversion and selectivity [17].

Results for oxidation of **15** under various reaction conditions are shown in Table 4. The oxidation of **15** in the presence of a catalytic amount of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid under oxygen atmosphere (1 atm) at 75°C for 6 h (standard conditions) produced adamantane-1-ol (**16**) (40%), adamantane-1,3-diol (**18**) (37%) along with a small amount of adamantane-2-one (**17**) (8%) (run 1). Leaving out $\text{Co}(\text{acac})_2$ from the reaction system led to a significant decrease of the yield of products (run 2). Needless to say, the oxidation did not promote by $\text{Co}(\text{acac})_2$ alone in the absence of NHPI (run 3). Oxidations of **15** using NHPI combined with $\text{Co}(\text{acac})_3$ or $\text{Co}(\text{OAc})_2$ gave almost the same results as those with $\text{Co}(\text{acac})_2$. Replacing of $\text{Co}(\text{acac})_3$ by $\text{Mn}(\text{acac})_3$ resulted in a decrease of the conversion of **15**. $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{OAc})_2$ were less efficient in this oxidation. On the basis of these

Table 4
Oxidation of adamantane (**15**) with dioxygen catalyzed by NHPI combined with metal salts ^a



Run	Metal Salt	Time (h)	Conv. (%)	Yield (%) ^b		
				16	17	18
1	$\text{Co}(\text{acac})_2$	6	93	43	8	40
2	—	6	17	53	—	—
3 ^c	$\text{Co}(\text{acac})_2$	6	no reaction			
4	$\text{Co}(\text{acac})_3$	6	91	47	8	37
5	$\text{Co}(\text{OAc})_2$	6	> 99	21	6	54
6	$\text{VO}(\text{acac})_2$	6	95	32	7	54
7	$\text{MoO}_2(\text{acac})_2$	6	85	54	6	27
8	$\text{Mn}(\text{acac})_3$	6	68	56	6	16
9 ^d	$\text{Co}(\text{acac})_2$	10	73	56	14	25
10	$\text{Co}(\text{acac})_2$	3	74	54	7	20
11	$\text{Co}(\text{acac})_2$	15	> 99	10	5	53

^a Adamantane (**15**) (3 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid (8 ml) at 75°C.

^b Determined by GLC based on **15** reacted.

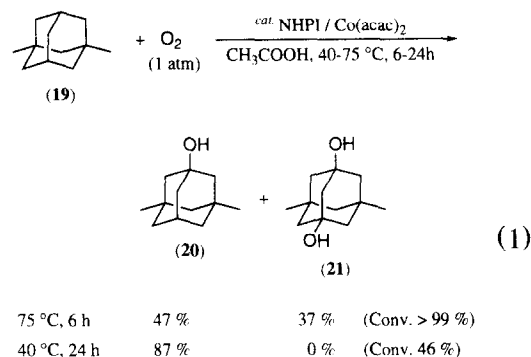
^c Reaction was conducted in the absence of NHPI.

^d Under air atmosphere.

results, **15** was allowed to react in the presence of NHPI (10 mol%) and Co(acac)₂ under several conditions. The oxidation of **15** in air under these conditions afforded **16** (41%), **17** (10%) and **18** (18%) in 73% conversion. When the reaction was prolonged for 15 h, diol **18** was obtained in 53% yield.

Since **18** is a very interesting material as a component of diols in polymer chemistry, stepwise hydroxylation of **16** was examined. The hydroxylation of **16** under the same conditions as the hydroxylation of **15** afforded **18** in 72% yield along with a small amount of adamantane-1,3,5-triol (17%). It has been reported that **18** is prepared by hydroxylation of **16** with ozone on silica gel in 43% or hydrolysis of 1,3-dibromoadamantane under basic conditions [18].

1,3-Dimethyladamantane (**19**) was also oxidized with dioxygen by NHPI in the presence or absence of Co(acac)₂. As we would expect, **19** was easier oxidized than **15** to form 3,5-dimethyladamantan-1-ol (**20**) (47%) and 5,7-dimethyladamantan-1,3-diol (**21**) (37%). No oxidation of a methyl group of **19** occurred under these reaction conditions. Oxidation of **19** at 40°C for 24 h gave **20** in high selectivity (87%), although the conversion was relatively low (46%),



2.4. Oxidation of alkylbenzenes with dioxygen catalyzed by NHPI combined with Co(acac)₂

Various alkylbenzenes are known to be oxidized with dioxygen in the presence or absence of transition metals [1,2].

The oxidation of several alkylbenzenes with dioxygen was attempted using the NHPI/Co(acac)₂ system (Table 5). The oxidation of toluene with NHPI (10 mol%) in the presence of Co(acac)₂ (0.5 mol%) in acetic acid in an oxygen atmosphere at 100°C for 6 h exclusively gave benzoic acid (> 99%) at 92% conversion (run 1). The same oxidation by NHPI alone produced only a trace amount of benzoic

Table 5

Oxidation of alkylbenzenes with dioxygen catalyzed by the NHPI/Co(acac)₂ system^a

Run	Substrate	Conv. (%)	Yield (%) ^b
1	toluene	92	benzoic acid (99)
2	<i>p</i> - <i>tert</i> -butyltoluene	97	<i>p</i> - <i>tert</i> -butylbenzoic acid (95)
3	<i>p</i> -methoxytoluene	98	<i>p</i> -methoxybenzoic acid (85)
4	ethylbenzene	91	acetophenone (93)
5	<i>n</i> -butylbenzene	90	1-phenyl-1-butanone (67)
6	<i>p</i> -xylene	94	<i>p</i> -toluic acid (78) + terephthalic acid (15)
7 ^{c,d}	<i>p</i> -xylene	99	<i>p</i> -toluic acid (23) + terephthalic acid (68)
8	<i>o</i> -xylene	92	<i>o</i> -toluic acid (80) + phthalic acid (14) ^e
9	cumene	31	acetophenone (54) + 2-phenyl-2-propanol (10) + phenol (17)

^a Substrate (5 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and Co(acac)₂ (0.5 mol%) in acetic acid (12.5 ml) at 100°C for 6 h.

^b Based on substrate reacted.

^c NHPI (20 mol%) was used.

^d Reaction was carried out at 100°C for 12 h.

^e Yield of dicarboxylic acid was estimated as dimethyl ester after esterification with excess methanol.

acid. Toluene has been reported to be oxidized with air in the presence of cobalt(II) 2-ethylhexanoate at 140–190°C and up to 10 atm of pressure to give benzoic acid in about 80% yield at 40–65% conversion [13]b. Consequently, the NHPI/Co(acac)₂ system is thought to be a useful catalytic system for the aerobic oxidation of toluene. Similarly, *p*-tert-butyltoluene and *p*-methoxytoluene were oxidized to *p*-tert-butylbenzoic acid and *p*-methoxybenzoic acid, respectively, in good yields (runs 2 and 3). In the oxidation of ethylbenzene, acetophenone was obtained in good yield (run 4). *n*-Butylbenzene was likewise oxidized to give 1-phenyl-1-butanone in slightly lower selectivity (67%). To evaluate the potential for the oxidation of the disubstituted alkylbenzenes, the oxidation of xylene was examined. *p*-Xylene was converted into the corresponding mono- and dicarboxylic acids, *p*-toluic acid and terephthalic acid, the ratio of which depended on the reaction time. The oxidation of *p*-xylene under the standard conditions gave *p*-toluic acid in 78% selectivity with 94% con-

version. When the reaction time was prolonged to 12 h, terephthalic acid was obtained in 68% yield. However, it was difficult to convert *o*-xylene to phthalic acid in high selectivity (run 8). Cumene is known to be oxidized by dioxygen to give cumene hydroperoxide, which is converted to phenol and acetone [19]. However, cumene was oxidized with difficulty by the NHPI/Co(acac)₂ system to form acetophenone (54%), 2-phenyl-2-propanol (10%) and phenol (17%) in 31% conversion. The low conversion of cumene was due to the formation of phenol. In fact, the oxidation of cumene in the presence of phenol (1 mol%) was markedly inhibited, and only trace amounts of products were formed.

2.5. Oxidation of alcohols with dioxygen catalyzed by NHPI combined with Co(acac)₃

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most frequently used transformations in organic synthesis, and numerous methods have been developed for this purpose [20]. In recent

Table 6
Oxidation of various alcohols with dioxygen catalyzed by the NHPI/Co(acac)₃ system^a

Run	Substrate	Time (h)	Conv. (%)	Yield (%) ^b
1 ^c	2-octanol (22)	20	9	2-octanone (> 99) (23)
2	22	20	93	23 (> 99)
3 ^d	22	20	< 1	23 (trace)
4	1-octanol (24)	5	90	octanoic acid (96) (25)
5 ^c	24	20	75	25 (95)
6	1-hexanol	5	91	hexanoic acid (92)
7	2-methyl-1-pentanol	5	86	2-methyl-1-pentanoic acid (94)
8 ^e	<i>trans</i> -2-hexen-1-ol	5	92	2-hexenoic acid (54) + butanoic acid (17)
9	1-octen-3-ol	5	89	1-octene-3-one (61)
10	cyclohexanol	15	96	cyclohexanone (92)
11	2-methyl-1-cyclohexanol	15	97	2-methyl-1-cyclohexanone (95)
12	cyclooctanol	15	95	cyclooctanone (82)
13	borneol	15	97	D-camphor (> 99)
14	L-menthol	15	78	L-menthone (68)
15	1-methyl-1-cyclohexanol	15	no reaction	

^a Substrate (5 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and Co(acac)₃ (0.5 mol%) at 75°C for 20 h in acetonitrile (10 ml).

^b Based on substrates reacted.

^c Reaction was conducted without Co(acac)₃.

^d Reaction was conducted without NHPI.

^e Reaction was conducted at 65°C.

years, there has been an increasing need for the selective aerobic oxidation of alcohols to carbonyl compounds under mild conditions, due especially to environmental reasons. There have been a few reports on the aerobic catalytic oxidation of alcohols [21]. However, methodology for the aerobic oxidation of alcoholic functions is still keenly sought to produce carboxylic acids and ketones.

Table 6 shows the representative results for the aerobic oxidation of various alcohols by NHPI combined with $\text{Co}(\text{acac})_3$. In contrast to the oxidation of benzylic compounds by dioxygen where the oxidations were prompted by a catalytic amount of NHPI (10 mol%) [10], secondary alcohols such as 2-octanol (**22**) were difficult to be oxidized by NHPI under these conditions (run 1). Fortunately, we found that **22** is smoothly oxidized to 2-octanone (**23**) by adding a slight amount of $\text{Co}(\text{acac})_3$ (0.05 equiv. with respect to NHPI) under oxygen atmosphere in acetonitrile at 75°C. Under these conditions, the oxidation of **22** by $\text{Co}(\text{acac})_3$ alone resulted in the recovery of the starting alcohol **22**. Although the oxidation of a primary alcohol such as 1-octanol (**24**) with dioxygen by NHPI (10 mol%) in acetonitrile at 75°C for 20 h produced octanoic acid (**25**) in 71% yield (in 75% conver-

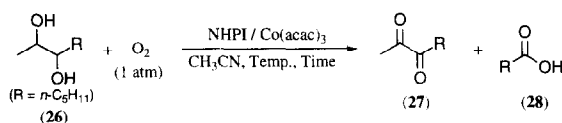
sion), the same oxidation was achieved in almost quantitative yield within 5 h by using the new catalytic system, NHPI combined with $\text{Co}(\text{acac})_3$. Similar results were obtained in the oxidation of 2-methyl-1-pentanol, *trans*-2-hexen-1-ol and 1-octen-3-ol. Aerobic oxidations of various cyclic alcohols by the NHPI/ $\text{Co}(\text{acac})_3$ system were also examined (runs 10–15). In these conditions, ketones were obtained in good yields except for L-menthone. The oxidation of a tertiary alcohol such as 1-methyl-1-cyclohexanol did not take place and the alcohol was recovered unchanged.

The conversion of *vic*-diols to diketones is usually achieved by metal oxidants such as AgCO_3 [22] or permanganate [23]. Recently, it has been reported that *vic*-diols can be oxidized via a catalytic process using the TEMPO–NaOCl system under electrochemical conditions [24] or using a hydrogen peroxide/PCWP system [25]. The oxidation of *vic*-diols to the corresponding dicarbonyl compounds with molecular oxygen is a desirable reaction in oxidation chemistry, since these transformations by aerobic oxidation are difficult to be carried out owing to the carbon–carbon bond cleavage of the diol part.

The aerobic oxidation of 2,3-octanediol (**26**)

Table 7

Oxidation of 2,3-octanediol (**26**) with dioxygen catalyzed by NHPI under various conditions ^a













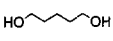
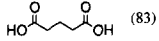




Run	NHPI (mol%)	$\text{Co}(\text{acac})_3$ (mol%)	Temp. (°)	Time (h)	Conv. (%)	Yield (%) ^b	
						27	28
1	10	—	75	20	11	46	0
2	10	2.0	75	10	99	59	30
3	10	2.0	65	16	98	65	27
4	20	2.0	65	12	97	77	15
5	—	2.0	65	12	5	trace	40

^a Substrate (2 mmol) was allowed to react with dioxygen (1 atm) in acetonitrile (8 ml).

^b Based on **26** reacted.

Table 8
Oxidation of various diols with dioxygen catalyzed by the NHPI/Co(acac)₃ system^a

Run	Substrate	Conv. (%)	Yield (%) ^b	
1 ^c		97	 (13)	 (86)
2		62	 (42)	 (48)
3		94	 (45)	 (47)
4 ^d		88	 (78)	 (19)
5 ^d		80	 (83)	
6 ^d		76	 (96)	

by NHPI/Co(acac)₃ was chosen as a model reaction and examined the system under several reaction conditions (Table 7).

The oxidation of **26** with dioxygen (1 atm) by NHPI (10 mol%) in acetonitrile at 75°C took place with difficulty to form 2,3-octanedione (**27**) in poor yield (5%), but the same oxidation by NHPI (10 mol%) combined with Co(acac)₃ (2 mol%) produced **27** in 58% yield along with a cleaved product, hexanoic acid (**28**) (30%). The employment of Co(acac)₂ in place of Co(acac)₃ resulted in a considerable decrease of products because of the formation of a complex of Co(acac)₂ with the diol **27**. When the reaction was conducted at 65°C for 12 h under these conditions, 75% yield of **27** was attained. Needless to say, Co(acac)₃ alone had little effect on the oxidation of **26** (run 5).

On the basis of these results, several diols were allowed to react under oxygen atmosphere by using the NHPI/Co(acac)₃ system in the selected reaction conditions (Table 8).

1,2-Diphenylethane-1,2-diol was oxidized to benzoin in 84% yield with a small amount of benzoin (14%). 1,2-Cyclohexanediol and 1,2-cyclooctanediol were difficult to be selectively oxidized to the corresponding 1,2-diketones because of the formation of dicarboxylic acids. However, 1,4-cyclohexanediol was converted into hydroxy ketone rather than diketone in good yield. α,ω -Diols such as 1,5-pentanediol gave dicarboxylic acid in 66% yield. 3-Methyl-2,4-hexanediol was oxidized to 4-hydroxy-3-methyl-2-hexanone with high selectivity.

3. Discussion

Masui et al. have suggested the formation of phthalimide *N*-oxyl (PINO) as the key species in the electrochemical oxidation of alcohols to ketones using NHPI as an electron carrier [26]. In order to confirm the formation of PINO, in the present work the NHPI-catalyzed aerobic oxidation, electron spin resonance (ESR) measurement was carried out under selected conditions. When benzonitrile solution of NHPI was exposed to dioxygen at 80°C for 1 h², the ESR spectrum attributed to PINO was clearly observed as a triplet signal based on hyperfine splitting (hfs) by a nitrogen atom ($g = 2.0074$, $a_N = 0.43$ mT) (Fig. 1). The g -value and hfs constant observed for PINO was in fair agreement with those ($g = 2.0073$, $a_N = 0.423$ mT) reported by Mackor et al. [27]. Needless to say, no ESR signal was observed under argon. It is noteworthy that the PINO is easily formed by exposing NHPI to molecular oxygen under moderate conditions.

^a Substrate (2 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (20 mol%) and Co(acac)₃ (2 mol%) at 65°C for 12 h in acetonitrile (8 ml).

^b Based on substrate reacted.

^c Reaction was carried out at 75°C.

^d NHPI (10 mol%) and Co(acac)₃ (0.5 mol%) was used.

² ESR spectra were obtained under the following conditions: sweep width: 327 ± 2.5 mT; modulation: 0.1 mT; and microwave power: 1 mW. Benzonitrile containing 10^{-2} mmol of NHPI was allowed to expose under atmosphere oxygen at 80°C for 1 h. The air in the ESR tube was replaced by dioxygen gas by means of the freeze-pump-thaw-method. The ESR parameter was determined by using solid Mn²⁺ ($g = 2.034$) as a standard.

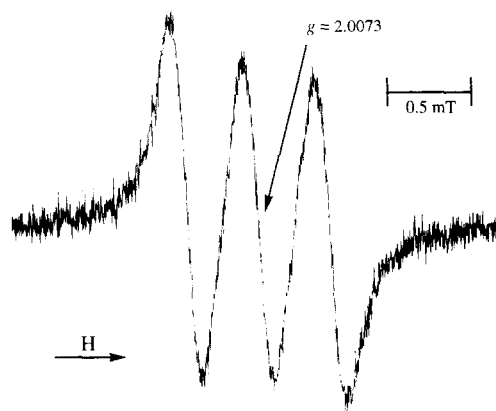
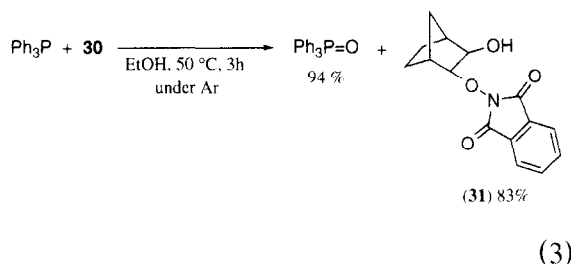
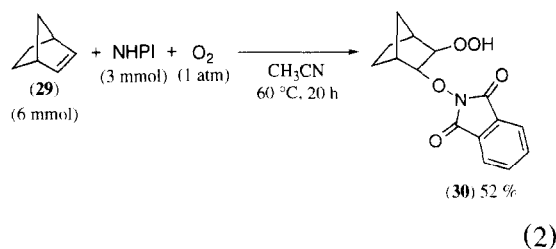


Fig. 1. ESR spectrum of phthalimide *N*-oxyl radical (PINO) under dioxygen in acetonitrile at 80°C.

Furthermore, 2-norbornene (**29**) was allowed to react with NHPI under an oxygen atmosphere in acetonitrile at 60°C. The reaction gave *N*-(2-hydroperoxybicyclo[2.2.1]heptan-2-yloxy)-phthalimide (**30**) in 52% yield (Eq. 2). Treatment of triphenylphosphine with **30** produced triphenylphosphineoxide (94%) and *N*-(hydroxy-bicyclo[2.2.1]heptan-2-yloxy)phthalimide (**31**) (83%) (Eq. 3). This result definitely shows that the radical species, PINO, is smoothly generated from NHPI and molecular oxygen in the absence of transition metals under mild conditions. Hence, the oxidation process of alkanes such as cyclooctane (**7**), which is oxidized by dioxygen using NHPI alone, can be outlined as in Scheme 1. The first step of the reaction is thought to involve the generation of the PINO radical from NHPI and dioxygen. The resulting PINO abstracts a hydrogen atom from the substrates to form alkyl radicals, subsequent oxygenation of which by dioxygen produces peroxy radicals, which are converted to ketones and/or dicarboxylic acids. In some cases, intramolecular hydrogen abstraction by the resulting alkyl peroxy radical occurs, and leads to the formation of the diketone **9**.



Unfortunately, we are currently unable to clearly explain the role of $\text{Co}(\text{acac})_n$ as a co-catalyst in NHPI-catalyzed aerobic oxidation. However, we can make several proposals which seem to agree with the experimental results.

To gain additional insight into NHPI/ $\text{Co}(\text{acac})_2$ -catalyzed aerobic oxidation, the absorption rate of dioxygen during the oxidation of ethylbenzene (**32**) to acetophenone (**33**) with several catalytic systems was measured using a constant-pressure absorption apparatus. Fig. 2 shows the time-dependence curves of the O_2 uptake of **32** under atmospheric pressure (1 atm) at 80°C. It is interesting to compare the rate of O_2 uptake by **32** in the NHPI/ $\text{Co}(\text{acac})_2$ and NHPI/ $\text{Co}(\text{acac})_3$ systems. No induction period was observed in O_2 uptake by **32** with NHPI/ $\text{Co}(\text{acac})_2$, while that with the NHPI/ $\text{Co}(\text{acac})_3$ system did not occur until after about 1.5 h. This finding is in accord with the results of adding NHPI alone to $\text{Co}(\text{acac})_2$ or $\text{Co}(\text{acac})_3$. When NHPI was added to an acetic acid solution of $\text{Co}(\text{acac})_2$, the color of the solution immediately changed from pink to violet, and a mixture of several complexes (**A**) was obtained. On the other hand, the same procedure with $\text{Co}(\text{acac})_3$ led to no color change of the solution, and most of the starting materials were recovered unchanged. However, when **32** was added to this solution, the color of the

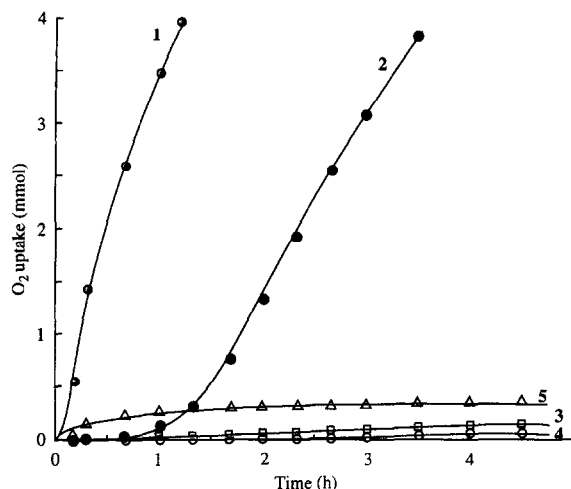


Fig. 2. Time dependence curves of O_2 uptakes for the oxidation of ethylbenzene (**32**) under atmospheric pressure of dioxygen by various catalysts. Conditions: Ethylbenzene (**32**) (10 mmol) was allowed to react with dioxygen (1 atm) in acetic acid (25 ml) at 80°C . (1) NHPI (10 mol%), $\text{Co}(\text{acac})_2$ (0.5 mol%). (2) NHPI (10 mol%), $\text{Co}(\text{acac})_3$ (0.5 mol%). (3) NHPI (10 mol%). (4) $\text{Co}(\text{acac})_2$ (0.5 mol%). (5) AIBN (5 mol%), $\text{Co}(\text{acac})_2$ (0.5 mol%).

solution gradually changed to violet and finally became the same as that in the NHPI/ $\text{Co}(\text{acac})_2$ system to form complexes (**A**) similar to those derived from NHPI and $\text{Co}(\text{acac})_2$. This result indicates that $\text{Co}(\text{acac})_3$ is gradually reduced to $\text{Co}(\text{II})$ with **32** via a well-known one-electron transfer process³, and the resulting $\text{Co}(\text{II})$ species readily reacts with NHPI to produce complexes similar to those derived from the NHPI/ $\text{Co}(\text{acac})_2$ system. These results well reflect the differences in the induction period between the NHPI/ $\text{Co}(\text{acac})_2$ and NHPI/ $\text{Co}(\text{acac})_3$ systems during O_2 uptake by **32**. The induction period of 1.5 h observed with the NHPI/ $\text{Co}(\text{acac})_3$ system may represent the time required to reach a threshold concentration of $\text{Co}(\text{II})$ by one-electron transfer from **32** to $\text{Co}(\text{III})$. Almost no O_2 uptake was observed in the oxidation of **32** by NHPI, $\text{Co}(\text{acac})_2$, or $\text{Co}(\text{acac})_3$ alone. In the same oxidation using the AIBN/ $\text{Co}(\text{acac})_3$ and NHPI/AIBN sys-

³ The oxidation of alkylbenzenes [28] and cyclohexane [29] by $\text{Co}(\text{III})$ ion is known to involve one-electron transfer from substrates to $\text{Co}(\text{III})$, yielding $\text{Co}(\text{II})$ ion and radical cations.

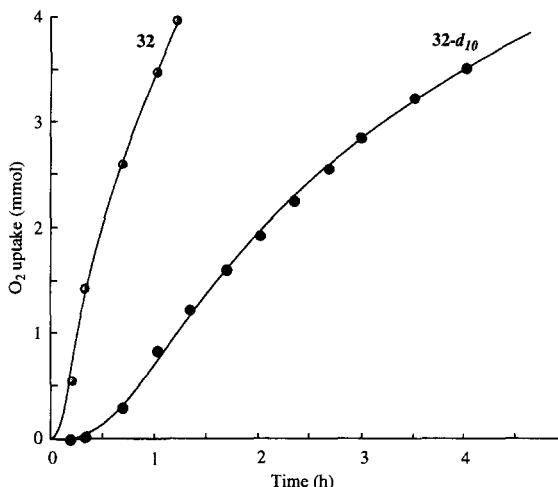
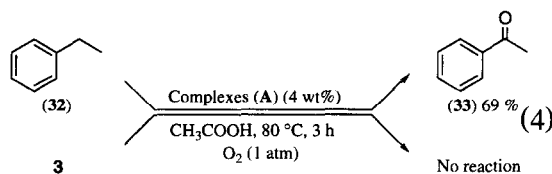


Fig. 3. Time dependence curves of O_2 uptakes for the oxidation of ethylbenzene (**32**) and ethylbenzene- d_{10} (**32-d₁₀**) with dioxygen catalyzed by the NHPI/ $\text{Co}(\text{acac})_2$ system. Conditions: Ethylbenzene **32** (10 mmol) was allowed to react with dioxygen (1 atm) in the presence of NHPI (10 mol%) and $\text{Co}(\text{acac})_2$ (0.5 mol%) in acetic acid (25 ml) at 80°C .

tems, the results were almost the same except for O_2 uptake in the early stage of the reaction by radicals generated from AIBN. The isotope effect during the present oxidation was estimated by measuring the oxygen uptake by ethylbenzene (**32**) and ethylbenzene- d_{10} (**32-d₁₀**) (Fig. 3). The observed isotope effect, k_H/k_D , was approximately 3.74. In addition, the oxidation of **32** in the presence of hydroquinone (1 mol%) under the standard conditions did not occur at all. These results strongly suggest that the present aerobic oxidation proceeds via a reaction pathway similar to that in free radical autoxidation.

On the other hand, **32** and cyclohexane **3** were oxidized using the complexes **A** obtained from NHPI and $\text{Co}(\text{acac})_2$ (Eq. 4). **32** was oxidized to acetophenone in 69% yield, while **3** failed to be oxidized by the complexes **A**,



Although the role of the Co(II) species in the NHPI-catalyzed aerobic oxidation is not fully understood, the Co(II) species may be related to the generation of the phthalimide *N*-oxyl radical PINO from NHPI. Indeed, PINO was readily observed when a very small amount of Co(acac)₂ (0.005 mol% with respect to NHPI) to the NHPI solution in benzonitrile at 80°C was added. However, no such effect was observed when Co(acac)₃ was added to the NHPI solution.

4. Experimental

¹H and ¹³C NMR were measured at 270 and 67.5 MHz, respectively, with tetramethylsilane as an internal standard. Infrared (IR) spectra were measured using NaCl or KBr pellets. A GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). Oxygen-absorption rates were measured with an isobaric gas-absorption apparatus under a closed-flow system (2 ± 0.1 l oxygen/h) equipped with an electrolyzer. ESR measurements were performed on a JEOL-FE-1X (X-band) with 100 kHz field modulation.

All starting materials and catalysts were purchased from commercial sources and used without further treatment. The yields of products were estimated from the peak areas based on the internal standard technique.

4.1. General procedure for oxidation of benzylic and hydroaromatic compounds

An benzonitrile (5 ml) solution of substrates (2 mmol), NHPI (32 mg, 10 mol%) was placed in a three-necked flask equipped with a balloon filled with O₂. The mixture was stirred at 100°C for 20 h. After removal of the solvent under reduced pressure, the products were purified by column chromatography on silica gel to give the corresponding oxygenated products.

4.2. General procedure for oxidation of cycloalkanes and polycyclicalkanes

An acetic acid (12.5 ml) solution of cycloalkane (5 mmol), NHPI (82 mg, 10 mol%), and Co(acac)₂ (7.5 mg, 0.5 mol%) was placed in a three-necked flask equipped with a balloon filled with O₂. The mixture was stirred at 100°C for 6 h. After removing the solvent under reduced pressure, methanol (25 ml) and a catalytic amount of conc. H₂SO₄ were added to the resulting mixture and stirred at 65°C for 15 h. The resulting solution was extracted with diethyl ether (20 ml × 3). The combined extracts were dried over anhydrous MgSO₄. Removal of solvent under reduced pressure gave a clean liquid, which was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 5/1) to give the corresponding oxygenated products.

4.3. General procedure for oxidation of alkylbenzenes

An acetic acid (12.5 ml) solution of alkylbenzenes (5 mmol), NHPI (82 mg, 10 mol%), and Co(acac)₂ (7.5 mg, 0.5 mol%) was placed in a three-necked flask equipped with a balloon filled with O₂. The mixture was stirred at 100°C for 6 h. After removal of the solvent under reduced pressure, the products were purified by column chromatography on silica gel to give the corresponding oxygenated products.

4.4. General procedure for oxidation of alcohols

An acetonitrile (10 ml) solution of alcohols (5 mmol), NHPI (82 mg, 10 mol%), and Co(acac)₃ (7.5 mg, 0.5 mol%) was placed in a three-necked flask equipped with a balloon filled with O₂. The mixture was stirred at 75°C for 20 h. After removal of the solvent under reduced pressure, the products were purified by column

chromatography on silica gel to give the corresponding oxygenated products.

4.5. General procedure for measuring oxygen-absorption rates

Oxygen-absorption rates were measured with an isobaric gas-absorption apparatus in a closed-flow system (2 ± 0.1 l oxygen/h) equipped with an electrolyzer using 25 ml of acetic acid containing ethylbenzene (1.06 g, 10 mmol), NHPI (163 mg, 10 mol%) and Co(acac)₂ (14.7 mg, 0.5 mol%) at 80°C. Oxygen absorption was periodically measured in the constant-pressure closed system.

4.6. Reaction of **29** with NHPI

An acetonitrile (5 ml) solution of 2-norbornene (564 mg, 6 mmol) and NHPI (489 mg, 3 mmol) was placed in a three-necked flask equipped with a balloon filled with O₂. The mixture was stirred at 60°C for 20 h. After the reaction, acetonitrile was removed under reduced pressure to give a white crystal, which was purified by diethyl ether (30 ml) to give the hydroperoxide (**30**) in 52% yield.

4.6.1. *N*-(2-hydroperoxybicyclo[2.2.2]heptan-2-yloxy)phthalimide (**30**)

¹H NMR (CDCl₃) δ 1.16–1.41 (m, 2H), 1.48–1.65 (m, 2H), 2.04 (d, *J* = 10.0 Hz, 1H), 2.31 (s, 1H), 2.94 (s, 1H), 4.14 (d, *J* = 5.3 Hz, 1H), 4.36 (d, *J* = 5.3 Hz, 1H), 7.79–8.55 (m, 4H), 10.65 (s, 1H). ¹³C NMR (CDCl₃) δ 22.9, 25.9, 33.6, 39.8, 41.7, 89.0, 93.6, 123.9, 128.6, 134.9, 164.3. IR (KBr) 3381, 2950, 1789, 1732, 1379, 1188, 993, 878, 699, 520 cm⁻¹. Calcd for C₁₅H₁₅NO₅: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.17; H, 5.18; N, 4.82.

4.7. Reaction of **30** with triphenylphosphine

An ethanol (30 ml) solution of **30** (289 mg, 1 mmol) and Ph₃P (262 mg, 1 mmol) was placed in a three-necked flask and the mixture was

stirred at 50°C for 3 h under an Ar atmosphere. After the reaction, ethanol was removed under reduced pressure to give a white crystal, which was purified by diethyl ether (30 ml) to give triphenylphosphine oxide in 94% yield along with alcohol **31** (83%).

4.7.1. *N*-(2-hydroxybicyclo[2.2.2]heptan-2-yloxy)phthalimide (**31**)

¹H NMR (CDCl₃) δ 1.05–1.12 (m, 3H), 1.21 (d, *J* = 10.5 Hz, 1H), 1.46–1.63 (m, 4H), 2.05 (d, *J* = 10.5 Hz, 1H), 2.29 (s, 1H), 2.66 (s, 1H), 3.91 (s, 1H), 4.00 (s, 1H), 7.75–7.87 (m, 4H), 10.65 (s, 1H). ¹³C NMR (CDCl₃) δ 24.0, 24.9, 32.7, 41.3, 43.2, 75.8, 93.2, 123.7, 128.6, 134.7, 164.0; IR (KBr) 3451, 2964, 1783, 1730, 1379, 1186, 999, 878, 782, 703, 518 cm⁻¹.

These values were consistent with those reported in the literature [30].

4.8. Preparation of complexes (A)

A mixture of NHPI (294 mg, 2 mmol) and Co(acac)₂ (235 mg, 0.8 mmol) in acetic acid (15 ml) was stirred at 80°C under an oxygen atmosphere. After 0.5 h, the reaction mixture was evaporated and an orange solid was obtained. The resulting solid was washed using acetonitrile and then the complexes (A) were obtained (271 mg).

4.9. Oxidation of **3** and **32** catalyzed by complexes (A)

To a stirred solution of complex (A) (21 mg, 4 wt%) in acetic acid (10 ml) **3** or **32** was added (5 mmol), and the reaction mixture was fitted with a balloon filled with oxygen. The mixture was stirred at 80°C for 3 h. The workup was performed using the same method as previously described.

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